NOVEL SOLID AMINE SORBENTS AND APPLICATIONS FOR CARBON DIOXIDE REMOVAL

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ABSTRACT

In this paper, we report on our solid amine sorbent (HSC+) previously developed and used for space life support applications, which may also be of interest for CO_2 removal in greenhouse gas control and other industrial processes. Adsorption capacities of the material for CO_2 pick up were determined, and long term test data show excellent performance. In addition, we have determined the heat of adsorption associated with CO_2 pickup by HSC+ and the effect of moisture, using isothermal flow calorimetry. We have also performed thermal gravimetric analyses on the materials to gain insight into the stability of the material and determine the temperatures at which CO_2 and constituents of HSC+ desorb from the surface.

INTRODUCTION

In order for CO_2 capture to be implemented as a method for climate change mitigation, technologies must be developed that are efficient, cost-effective, environmentally benign, and easily applicable. Liquid amines, used as sorbents for removing CO_2 in the natural gas industry for roughly 50 years, represent the primary competing commercial technology (lowest cost to date). However, there are several disadvantages in the use of liquid amines[1]:
- High temperatures are required for regeneration (typically 100-120 °C)
- Equipment costs and maintenance for pumping or spraying liquids
- Corrosive effects of liquid amines and byproducts (corrosion inhibitors and high maintenance costs required); particularly accelerated by contaminants and acid gases
- Loss of amine due to evaporation (continual maintenance) and latent energy penalty
- Difficulty in handling liquids (as compared to solids)
- Amines must typically be maintained at <20% (occasionally up to 30%) concentration (to reduce corrosion), thereby compromising CO_2 removal capacity[2,3]
- Additives are required to prevent foaming; and
- Oxygen typically has to be limited to prevent reaction with the solvent[3] (<8%)

The focus of our work has been on solid amine sorbents[4-6], originally developed for space life support systems, but with several key advantages rendering them attractive for other applications: high capacity, low regeneration costs, long-term stability, intrinsically fast kinetics, no need for moisture removal from gas stream, and ease of handling. Through our Hamilton Sundstrand Space Systems International (HSSSI) Division, we previously developed a regenerable sorbent consisting of solid amine beads, known as HSC+. This material contains a liquid amine bonded to a high surface area, solid acrylic-based, polymeric support, followed by a coating to enhance the rate of CO_2 adsorption and desorption. Because a solid bed of material is used instead of liquids, there is minimal corrosion, and no equipment is needed to circulate or spray liquids. Our original use was for removing low concentrations of CO_2 at atmospheric pressure (typically less than 1%) and thus a key advantage is applicability to either high or low CO_2 partial pressures- i.e., compression of waste gas such as flue gas above atmospheric pressures is not mandatory. In addition, the sorbent may be made from low cost, commercially available amines and

the consumer cost is anticipated to be roughly the same as that for conventional liquid amines. Due to the anticipated long term stability of the material, periodic addition of amine, which is a necessity in conventional liquid amine systems, should not be required.

In order to design sorbents with higher capacities and favorable kinetics, a detailed study of the currently used sorbent, HSC$^+$ is essential. In this paper, we report on a preliminary experimental investigation of thermodynamic data for HSC+ such as heats of adsorption, adsorption capacity, and thermal gravimetric analyses. Due to the exothermic nature of the CO_2 absorption reaction and the variability of CO_2 capacity with temperature, physical property data is essential to optimize system parameters (power, weight and volume). Our overall goal is to maximize the cyclic CO_2 capacity of the system while adhering to system power, weight and volume specifications. By reporting on fundamental property data, this sorbent may also be found applicable for other CO_2 removal processes as well.

EXPERIMENTAL

The adsorption capacity for CO_2 and temperature increase associated with adsorption was determined using a flow apparatus, consisting of a pyrex tube packed with HSC$^+$. A thermocouple was placed at the center of the bed, the concentration of CO_2 was measured at the inlet and exit of the tube using an infra red detector (Horiba, model PIR-2000), and the mass of the tube was measured after equilibrium to determine equilibrium adsorption capacities. In order to determine the thermal stability of HSC$^+$, thermal gravimetric methdds (TA Instruments, model 2950) were used. All TGA experiments were taken under consistent conditions and typical sample sizes varied between 20 and 50 mg. The runs were initiated at room temperature (approximately 25°C), and the temperature was increased at a ramp rate of 10°C per minute. Nitrogen was used as a purge gas at a flow rate of roughly 70 ml/min throughout all experiments. We have also measured heats of adsorption using isothermal flow microcalorimetery. This highly sensitive technique is valuable for thermochemical measurements in which equilibrium is attained in a relatively short time. Rather than maintaining adiabatic conditions (i.e., eliminating heat flow to or from the sample cell), we maintain isothermal conditions and measure heat flow to or from the cell. Integration of the heat flow over the time period of the adsorption process provides the heat of adsorption. The instrument (CSC, model 4400) is a differential (dual cell) unit and can measure heat flows as low as 0.1 μW (25 nanocalories/sec). Operating temperatures range from 0 to 100 °C with an adsorbent bed volume of approximately 3 cm^3.

RESULTS

Figure 1 shows a typical breakthrough curve using an initial mass of 11.4 g of HSC$^+$, packed in a 1 inch-diameter tube. The flow rate of CO_2 (2% in N_2) was varied between ~0.5 and 2 slpm. The maximum temperature determined in the center of the bed was 53 °C, and the maximum adsorption capacity was found to be roughly 4% by mass. These experiments employed a bed packed solely with beads of HSC$^+$, whereas in practical applications, the use of a reticulated aluminum foam provides several advantages: the foam acts as a heat transfer and a bed retention medium, allowing for small scale changes in sorbent size without introducing a short-circuit path for channeling. These features are also in-place with the full-scale cycling sorbent system on-board the space shuttle orbiters.

TGA (thermal gravimetric analysis) data allow us to determine the range of temperatures at which CO_2, the coating material, and the amine(s) leave the surface of HSC$^+$ under controlled conditions. As shown in Figure 2, the initial peak in the mass loss derivative curve (at ~ 60 °C) is due to removal of CO_2, with a maximum rate in mass loss between 60 and 70 °C. The second peak at ~ 200 °C is due to removal of both amine and coating.
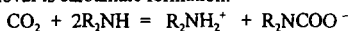
There is a change in the mechanism beginning at roughly 230 °C and complete decomposition occurs at ~ 450 °C. It is clear that loss of additional components (e.g., amine or coating) do not begin to take place until over 100 °C, illustrating thermal stability under the operating conditions we employ for space life support systems.

Figure 3 shows heat of adsorption data for the adsorption of CO_2 (2% in air) on HSC^+. In this example, an approximately 0.6 g sample of HSC^+ was exposed to a 2% mixture of CO_2 in N_2, at a flow rate of 30 ml/min. The heat of adsorption was calculated to be -94 (±8) kJ/mol CO_2 which is consistent with results anticipated for amine + CO_2 reactions. The value we have reported is an average for 5 sample trials, and the mass % of CO_2 adsorbed is 3.7 (±0.4) %. One of the predominant sources of error is believed to be incomplete degassing to remove CO_2 and moisture, and absorption of CO_2/H_2O during material handling and sample transfer. Note that the heat of adsorption reported here represents a total heat of adsorption for adsorption of the maximum concentration of CO_2, rather than a differential or isosteric heat of adsorption for a specific CO_2 coverage.
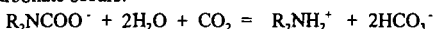
DISCUSSION

In order to design CO_2 scrubbers for various applications, detailed performance studies of the sorbent are essential. We have performed a set of preliminary experiments to determine thermophysical properties and reactivity of the solid amine sorbent HSC^+. Some of the key issues to address in designing improved sorbents are: capacity, ease of reversibility, and stability. TGA and capacity measurements have shown the material to be favorable for space life support applications although a detailed understanding of the mechanism is still lacking. This is the first report of a direct measurement of the heat of adsorption of CO_2 on the material which may provide insight into the mechanism and ease of reversibility of the process.
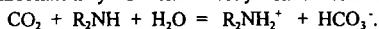
The mechanism for CO_2 removal using amines is known to be dependent on the presence of water[7,8]. Without moisture present, the main reaction believed to account for CO_2 removal is carbamate formation:
$$CO_2 + 2R_2NH = R_2NH_2^+ + R_2NCOO^-$$
This shows that for every one mole of amine, only ½ a mole of CO_2 is removed. However, when moisture is present, further reaction of the carbamate ion to form bicarbonate occurs:
$$R_2NCOO^- + 2H_2O + CO_2 = R_2NH_2^+ + 2HCO_3^-$$
Bicarbonate may also form directly from the amine + CO_2 + water reaction:
$$CO_2 + R_2NH + H_2O = R_2NH_2^+ + HCO_3^-.$$
Therefore, in the presence of water, one mole of amine is effective in removing one mole of CO_2. This mechanism has been discussed in the literature for several years[7]. In our results, based on a measurement of mass increase alone, it appears as if roughly 3 times more CO_2 is removed in the presence of water as compared to the absence of water. An additional possibility is that reaction on the surface, and/or moisture adsorption, allows more of the active sites of the material to be available for CO_2 removal.

Measuring heats of adsorption can also provide important information on the interaction between CO_2 and the sorbent. For the case of water vapor on HSC^+ ΔH was found to be − 47.2 (±1.0) kJ/mol H_2O, with nearly 17% mass capacity for water. As anticipated, a physisorptive process typically results in a ΔH similar to the heat of condensation of the adsorbed gas ($\Delta H \sim -44.0$ kJ/mol at 25 °C for water). The heat released during adsorption of CO_2 is significantly larger (-94 (±8) kJ/mol CO_2) than the heat of condensation of water vapor, indicative of a strong interaction between the CO_2 and the amine surface. An illustration of mechanistic differences is shown by the measurement of mass % adsorbed in the presence of water versus in the absence of water. In the case of a dry (CO_2, N_2 mixture), there is a 3.7 (± .4) % mass gain; while the gain is 16.8 (± 3.6)% in the case of

pure water vapor, and 27.3 (± 2.2)% in the case of CO_2 + water vapor. It is therefore clear that higher CO_2 capabilities are achieved by coadsorption of water. Future studies will investigate the mechanism by which coadsorption aids in carbon dioxide removal and on optimizing solid amine sorbents.

CONCLUSIONS

We have measured the equilibrium CO_2 adsorption capacity for HSC$^+$ to be ~ 4 % at ambient pressures, and have shown that the sorbent may be regenerated using vacuum desorption at ~ 1 Torr. Thermal gravimetric analysis was used to show that the amine is strongly bonded to the substrate and the material does not begin to lose amine/coating components until over 100 °C, while CO_2 is desorbed at roughly 60°C in a non pressure swing adsorption mode. The material has been tested for hundreds of cycles with no loss in performance.

ACKNOWLEDGEMENTS

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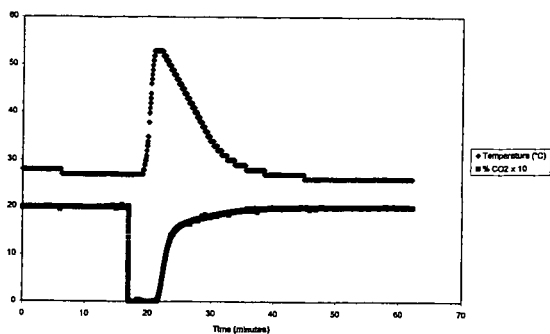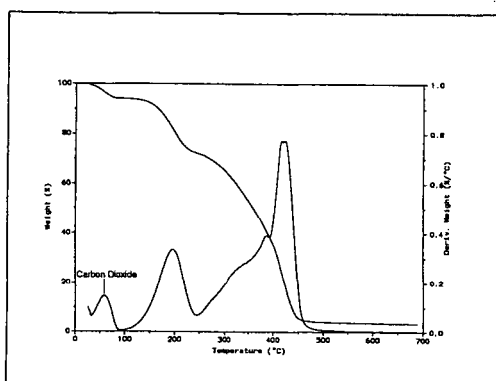Carbon Dioxide Concentration and Temperature Profiles

Figure 1.

TGA Data

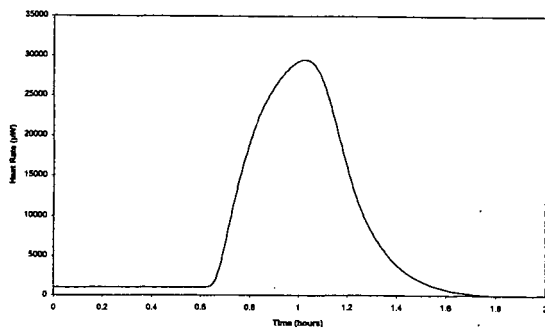Figure 2.

* HSC* + 2% CO_2 in N_2

Figure 3.

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